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METHODOLOGY • RESEARCH ARTICLE

Pesticide ecotoxicological effect factors and their uncertainties for freshwater ecosystems

Rosalie van Zelm · Mark A. J. Huijbregts · Leo Posthuma · Arjen Wintersen · Dik van de Meent

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Abstract
Background, aim, and scope Characterization factors for ecotoxicity in the Life Cycle Impact Assessment (LCIA) are used to convert emissions into ecotoxicological impacts. Deriving them involves a fate and an effect analysis step. The fate factor quantifies the change in environmental concentration per unit of emission, while the effect factor quantifies the change in impact on the ecosystem per unit of environmental concentration. This paper calculates freshwater ecotoxicological effect factors for 397 pesticides belonging to 11 pesticide-specific toxic modes of action (TMoA), such as acetylcholinesterase inhibition and photosynthesis inhibition. Moreover, uncertainties in the effect factors due to uncertain background concentrations and due to limited toxicity data are quantified.
Methods To calculate median ecotoxicological effect factors (EEFs), toxic pressure assessments were made, based on the species sensitivity distribution—and the multisubstance potentially affected fraction—concept. The EEF quantifies an estimate of the fraction of species that is probably affected due to a marginal change in concentration of a pesticide. EEFs were divided into a TMoA-specific and a chemical-specific part, which were calculated on the basis of physicochemical properties, emissions, and toxicity data. Propagation of parameter uncertainty in the EEFs and the TMoA- and chemical-specific parts was quantified by Monte Carlo simulation and results were reported as 90% confidence intervals.
Results Median EEFs range from $2{\cdot}10^{-3}$ to $7{\cdot}10^{6}$ l/g. Uncertainty in the TMoA-specific part is dominated by uncertainty in the TMoA-specific spread in species sensitivity and by uncertainty in the effective toxicity of a TMoA. Uncertainty in the chemical-specific part of the EEFs depends on the number of species for which toxicity data are available to calculate average toxicity (n_s) and ranges from a median uncertainty of 2.6 orders of magnitude for n_s=2 to one order of magnitude for $n_s \geq 4$. The TMoA-specific effect factor for systemic fungicides shows the largest uncertainty range. For seven TMoAs, uncertainty ranges of the TMoA-specific effect factor are less than two orders of magnitude. For the other four TMoAs, the EEF uncertainty range is between two and eight orders of magnitude. For the chemical-specific part of the EEFs, we found that variation in uncertainty readily decreases for pesticides for which toxicity data are available for at least three species.
Discussion The same parameters that contributed most to uncertainty were found for pesticides as were found before for high-production-volume chemicals. However, uncertainty in concentrations of pesticides was lower. TMoA-specific factors obtained with the applied nonlinear method differ up to nine orders of magnitude from the factor of 0.5, which is used in the linear method. With the applied method, a distinction in EEFs can be made among different TMoAs.
Conclusions Ecotoxicological effect factors are presented, including overviews of their uncertainty ranges and the main

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R. van Zelm (✉) · M. A. J. Huijbregts · D. van de Meent
Department of Environmental Science,
Institute for Water and Wetland Research,
Radboud University Nijmegen,
P.O. Box 9010, 6500 GL Nijmegen, The Netherlands
e-mail: r.vanzelm@science.ru.nl

L. Posthuma · A. Wintersen · D. van de Meent
Laboratory of Ecological Risk Assessment,
National Institute of Public Health and the Environment,
P.O. Box 1, 3720 BA Bilthoven, The Netherlands

contributors to uncertainty. The applied nonlinear method provides the possibility to quantify parameter uncertainty in the TMoA-specific part of the ecotoxicological effect factor, which is helpful to get more insight in how uncertainty in ecotoxicological characterization factors can be reduced.
Recommendations and perspectives The calculated uncertainty ranges can be included in life cycle assessment (LCA) case studies, which allows for better interpretation of LCA results obtained with the EEFs. To put the uncertainty in effect factors into perspective within LCIA, more information on the uncertainty in fate factors should be derived.

Keywords Ecotoxicity · Effect factor · Freshwater · LCIA · Pesticides · Potentially affected fraction · Toxic mode of action · Uncertainty

1 Background, aim, and scope

Characterization factors for ecotoxicity in the Life Cycle Impact Assessment (LCIA) describe the expected ecotoxicological impacts due to environmental emissions of toxic compounds. A fate and an effect analysis step are needed to obtain characterization factors (Margni et al. 2002; Rosenbaum et al. 2007; Schulze et al. 2001). The fate factor describes the change in environmental concentration per unit of emission. The effect factor addresses the change in impact on the ecosystem per unit rise of the compounds' environmental concentration, given the ambient concentration before the emission. This paper aims to derive ecotoxicological effect factors for pesticides and to include an analysis of uncertainties in their derivation.

Two main groups of methods are currently applied for the calculation of ecotoxicological effect factors, as discussed by various authors (Larsen and Hauschild 2007a; Pennington et al. 2004; Van de Meent and Huijbregts 2005): (a) linear methods, based on predicted no-effect concentrations (PNECs) and (b) nonlinear methods, based on toxic pressure assessments. Method (a) calculates effect factors as ratios of environmental concentrations over PNECs, and method (b) as potentially affected fractions of species (PAF). A PAF value quantifies the toxic pressure put on ecosystems due to the presence of a single chemical or a mixture of chemicals, and it reflects the fraction of all species that is expectedly exposed above a certain effect-related benchmark, such as the effect concentration for 50% of the species (EC50) or the no-observed-effect concentration (NOEC; De Zwart and Posthuma 2005). For mixtures, the estimated fraction is called the multisubstance PAF (msPAF). The main advantages of the PAF-approach over the PNEC approach are considered to be (1) the possibility to combine the potential impacts on ecosystems (a midpoint level), with a damage assessment that indicates the consequences of the potential impacts (an endpoint level) and (2) the possibility to model the effect of mixtures of chemicals on the environment (Goedkoop and Spriensma 1999; Huijbregts et al. 2002).

In a previous paper, ecotoxicological effect factors for high-production-volume chemicals (HPVCs), including uncertainties thereof, were calculated with the nonlinear msPAF method (Van Zelm et al. 2007). These HPVCs represented sets of compounds with rather nonspecific toxic modes of action (TMoAs). They are rather nonspecific as there are no specific aquatic taxa that are more sensitive to those chemicals than other taxa. Only few LCIA studies specifically focus on ecotoxicological impacts of pesticides (Antón et al. 2004; Juraske et al. 2007; Margni et al. 2002). The assessment of ecotoxicological impacts of pesticides, however, is specifically required in LCA case studies that focus on agriculture (Canals et al. 2006; Geisler et al. 2005; Humbert et al. 2007; Mouron et al. 2006; Van der Werf et al. 2005). In agricultural practice, pesticides are introduced into the environment with the explicit intention of exerting effects on one or more target organisms. Through intermedia transport, pesticides can reach parts of the environment outside from where they were initially released (De Zwart 2005; Verro et al. 2002).

The nonlinear method to derive ecotoxicological effect factors requires more information than the linear method. The uncertainty connected to the extra parameters introduced can be quantified well, in contradiction to the model uncertainty in the linear method. Previous LCA case studies show a relatively large uncertainty range for freshwater ecotoxicity, compared to other (nontoxic) impact categories (Geisler et al. 2005; Huijbregts et al. 2003). Geisler et al. (2005) state that, before the freshwater ecotoxicity impact scores are used in decision support, measures to reduce uncertainty have to be taken first. More insight therefore has to be gained into the main sources attributing to uncertainty.

This paper presents freshwater ecotoxicological effect factors for 397 pesticides, based on the msPAF method, with special interest in the role of toxic modes of action. Moreover, uncertainties in the effect factors due to uncertain background concentrations and due to limitations in the availability of ecotoxicity data are quantified. Results are discussed (1) in relation to the results obtained for HPVCs with a nonspecific TMoA, (2) in view of practical use in LCA, and (3) regarding future research that is needed to reduce uncertainties.

2 Methods

2.1 Effect factor calculations

The toxic pressure assessment method to calculate effect factors, as outlined by Van Zelm et al. (2007) for HPVCs, was applied in this study for pesticides. Lognor-

mal species sensitivity distributions (SSDs) were applied (Aldenberg and Jaworska 2000; Posthuma et al. 2002; Slob 1994; Van de Meent and Huijbregts 2005; Wagner and Løkke 1991).

Chemicals with different assumed major TMoAs are considered to act independently and do not influence each other's toxic mechanism. Effects in terms of the net toxic pressure of mixtures of emitted chemicals with different TMoAs can therefore be aggregated according to the mathematical model of response addition (Plackett and Hewlett 1952; Traas et al. 2002):

$$\mathrm{msPAF} = 1 - \prod_j \left(1 - \mathrm{PAF}_j\right) \quad (1)$$

where PAF_j is the potentially affected fraction of a mixture of chemicals with one TMoA j, and ms is multisubstance.

Chemicals with the same TMoA are considered to act independently but on the same receptor sites of toxic action. Exposure concentrations for such compounds, therefore, need to be aggregated according to mathematical rules of concentration addition. PAF j is therefore calculated by concentration addition over compounds with TMoA j (see Electronic Supplementary Material).

As the effect factor is defined by marginal changes in ecotoxicological effects due to marginal changes in production of goods and services, the ecotoxicological effect factor for pesticide x is obtained through partial differentiation of Eq. 1 over the concentration of pesticide x (C_x in grams per liter):

$$\frac{\partial \mathrm{msPAF}}{\partial C_x} = \left[\frac{\partial \mathrm{msPAF}}{\partial \mathrm{TU}_j}\right] \cdot \left[\frac{\partial \mathrm{TU}_j}{\partial C_x}\right] \quad (2)$$

The ecotoxicological effect factor consists of what can be called a TMoA-specific part ($\partial \mathrm{msPAF}/\partial \mathrm{TU}_j$) and a chemical-specific part ($\partial \mathrm{TU}_j/\partial C_x$). $\partial \mathrm{msPAF}/\partial \mathrm{TU}_j$ describes the change in overall toxic pressure put on an ecosystem due to a change in effective toxicity of a specific TMoA j (expressed in dimensionless toxic units TU_j). $\partial \mathrm{TU}_j/\partial \mathrm{C}_x$ expresses the toxic potency of a chemical, which describes the change in effective toxicity due to a change in concentration of one pesticide x. The subdivision of the ecotoxicological effect factor into a TMoA-specific and a chemical-specific part enables comparisons between chemicals with the same TMoA. If chemicals with the same TMoA are compared, solely the chemical-specific part needs to be investigated (Van Zelm et al. 2007).

The TMoA-specific part of the effect factor can be specified as follows:

$$\frac{\partial \mathrm{msPAF}}{\partial \mathrm{TU}_j} = f\left(\mathrm{msPAF}, \sigma_j, \mathrm{TU}_j\right) \quad (3)$$

where σ_j is the TMoA-specific spread in species sensitivity. Equation 3 is further specified in the Electronic Supplementary Material.

The chemical-specific part of the effect factor, or toxic potency of a chemical, is equal to:

$$\frac{\partial \mathrm{TU}_j}{\partial C_x} = \frac{1}{10^{\mu_x}} \quad (4)$$

where μ_x is the average sensitivity of species to pesticide x (g/l), with sensitivity being expressed as an NOEC, an EC50 or another ecotoxicity test end point.

2.2 Input data

To calculate the TMoA-specific part of the effect factor, emission estimates of 2004 for the Rhine–Meuse–Scheldt catchment area, physicochemical properties, and ecotoxicity data were obtained for 87 pesticides that represent 11 assumed major TMoAs (Henning-de Jong et al. 2008). Some pesticides can have applications outside agriculture, such as weed control in industry or in public areas, the emissions of which were not taken into account in this study. Expected ambient concentrations in the freshwater environment at steady-state, according to the use pattern of 2004, were predicted with SimpleBox 3.0 (Den Hollander et al. 2004), which is the underlying fate model of the European Union System for the Evaluation of Substances (Vermeire et al. 2005). In its default settings, the regional scale in SimpleBox is represented by a simplified model of the rivers Rhine, Meuse, and Scheldt.

The toxic potency ($\partial \mathrm{TU}/\partial \mathrm{C}$) could be calculated for 397 pesticides (Table 1). This selection of pesticides was made based on information on TMoA and availability of aquatic toxicity data. Data on TMoA were derived from Henning-de Jong et al. (2008), De Zwart (2005), ASTER (USEPA 2004), and e-toxBase (RIVM 2008). The required toxicity data were

Table 1 Number of pesticides (N) per major toxic mode of action for which ecotoxicological effect factors were calculated

Toxic mode of action	Abbreviation	Number
Inhibition of acetylcholinesterase: organophosphates	IAO	121
Inhibitor of photosynthesis	IP	56
Inhibition of acetylcholinesterase: carbamates	IAC	41
Plant growth regulator	PGR	40
Neurotoxicant: pyrethroids	NP	35
Plant growth inhibitor	PGI	26
Inhibitor of ergosterol synthesis	IES	24
Systemic fungicide	SF	21
Inhibitor of amino acid synthesis	IAS	12
Dithiocarbamates	DTC	11
Inhibitor of cell division	ICD	10

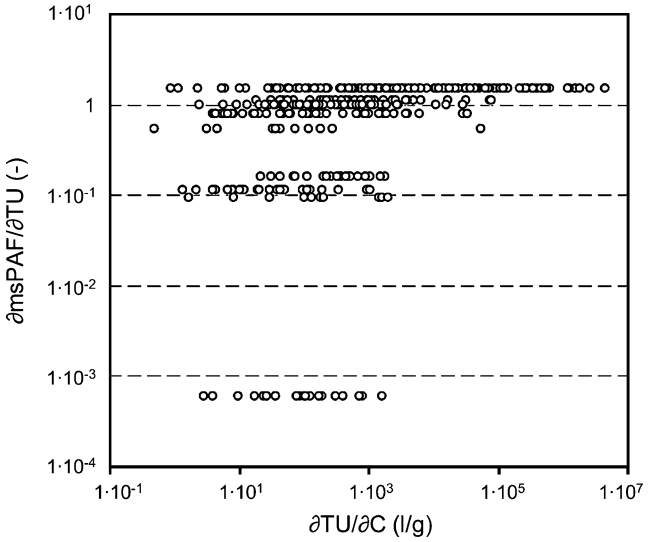

Fig. 1 The toxic mode of the action-specific part of the effect factor (∂msPAF/∂TU) versus the toxic potency (∂TU/∂C)

derived from ecotoxicity test data exported from e-toxBase (RIVM 2008), taking acute EC50s as input data to derive their SSDs. For every pesticide, average EC50s per species were taken to prevent species with a large number of test data to be overrepresented in SSD modeling.

To indicate to which species groups the species belong of which toxicity tests were included in the EC50 calculations, each species was assigned to one of the following four species groups: (1) bacteria, archaea, and protista; (2) plantae and fungi; (3) invertebrata; and (4) vertebrata ectotherm. The number of toxicity tests available per species group for each pesticide is indicated in the Electronic Supplementary Material.

2.3 Uncertainty analysis

Propagation of parameter uncertainty in the ecotoxicological effect factors and the TMoA-specific and chemical-specific parts was quantified by means of Monte Carlo simulation. This yielded uncertainty distributions for each output variable. The Monte Carlo simulations consisted of 10,000 iterations and were performed with Latin hypercube sampling using Crystal Ball 7.1.2 (Decisioneering Inc. 2005). An uncertainty importance analysis, based on rank correlation, was done to identify the contribution to uncertainty of each parameter in the ecotoxicological effect factor.

According to Eqs. 3 and A1 in the Supporting Information, three variables can be distinguished as potential contributors to uncertainty in the TMoA-specific part of the effect factor: msPAF, TU_j, and σ_j; these variables may be (in part) correlated. Uncertainty in msPAF was assumed to follow a uniform distribution between $5{\cdot}10^{-5}$ and $5{\cdot}10^{-1}$, following Van Zelm et al. (2007), taking into account that msPAF cannot be larger than the potentially affected fraction of species of a TMoA *j*. Uncertainty in effective toxicity TU_j is defined by uncertainty in the concentrations of pesticides and in average species sensitivity to all pesticides that contribute to a TMoA *j*. Uncertainty in estimated ambient freshwater concentrations due to uncertainty in physicochemical parameters and uncertainty in emission profiles was quantified by performing a Monte Carlo simulation in SimpleBox 3.0, using data from Henning-de Jong et al. (2008). Simulated freshwater concentrations were fitted to chemical-specific lognormal distributions and used as input in the uncertainty analysis of the ecotoxicological effect factors. Uncertainty in average sensitivity (μ_x) depends on the chemical-specific spread in species sensitivity (σ_x) and the number of species for which toxicity data were available (n_s). Uncertainty in the TMoA-specific spread in species sensitivity (σ_j) depends on uncertainty in chemical-specific spreads in species sensitivities to all pesticides belonging to one major TMoA and the number of pesticides (*N*) included in the calculations. Further details about uncertainty distributions of μ_x, σ_x, and σ_j can be found in the Supporting Information.

3 Results

Median ecotoxicological effect factors for the 397 pesticides range from $2{\cdot}10^{-3}$ to $7{\cdot}10^{6}$ l/g. Propamocarb hydrochloride, a systemic fungicide, causes the least toxic pressure per unit concentration increase, while tefluthrin, a pyrethroid neurotoxicant, causes the largest freshwater toxic pressure per unit concentration increase.

Figure 1 shows the median values of the estimated toxic potency (∂TU/∂C) for each pesticide and the median values of the TMoA-specific part of the effect factor (∂msPAF/∂TU). According to Fig. 1, ∂TU/∂C and ∂msPAF/∂TU are not related. Median values of ∂msPAF/∂TU range from $6.1{\cdot}10^{-4}$ to 1.5. Systemic fungicides cause the lowest ecological response per toxic unit added to the environment, and pyrethroid neurotoxicants and inhibitors of acetylcholinesterase (organophosphates) cause the largest response per toxic unit added. Median freshwater toxic potency values (∂TU/∂C) range from $5{\cdot}10^{-1}$ l/g for sulfometuron methyl, an inhibitor of amino acid synthesis, to $4{\cdot}10^{6}$ l/g for tefluthrin. Ecotoxicological effect factors and TMoA-specific and chemical-specific parts for each pesticide included are listed in the Electronic Supplementary Material.

Figure 2 shows the median TMoA-specific parts of the ecotoxicological effect factors (∂msPAF/∂TU), with their 90% confidence intervals. These 90% confidence intervals range from eight orders of magnitude for systemic fungicides (SF) to a factor of 2.0 for dithiocarbamates

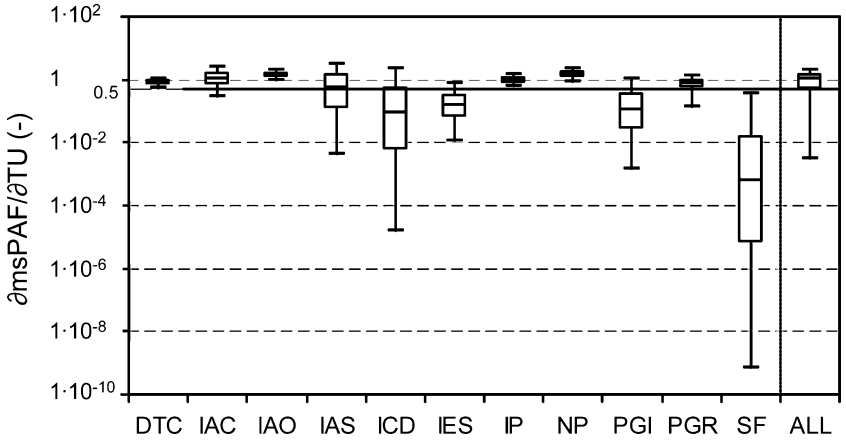

Fig. 2 Box plots of the TMoA-specific part of the effect factor (∂msPAF/∂TU) for 11 TMoAs and the weighted average. The *center* of each *box* equals the median value, the edges of each box the 25th and 75th percentiles, and the whiskers the fifth and 95th percentiles to represent uncertainty in ∂msPAF/∂TU. The *line* displays the TMoA-specific part of the effect factor used in the linear (PNEC-based) assessment method to derive ecotoxicological effect factors (see text)

(DTC). The weighted average of ∂msPAF/∂TU (ALL), using the number of pesticides per TMoA as a weighting factor, equals 1.1 effect units per toxic unit added and has a 90% confidence interval of two orders of magnitude. TMoA-specific input parameters, with their 90% confidence intervals, are given in the Electronic Supplementary Material. For comparison to the ratio-based (PNEC) assessments, Fig. 2 contains the uniform value of 0.5, used as TMoA-specific part of the effect factor in the ratio-based method, as applied by Payet (2004) and Pennington et al. (2004). An overview of each main contributor to uncertainty in ∂msPAF/∂TU is outlined in Table A2 of the Electronic Supplementary Material. Uncertainty in msPAF and uncertainty in the TMoA-specific spread in species sensitivity σ_j dominate uncertainty of ∂msPAF/∂TU compared to uncertainties in average sensitivity μ_x and in the concentration of pesticides.

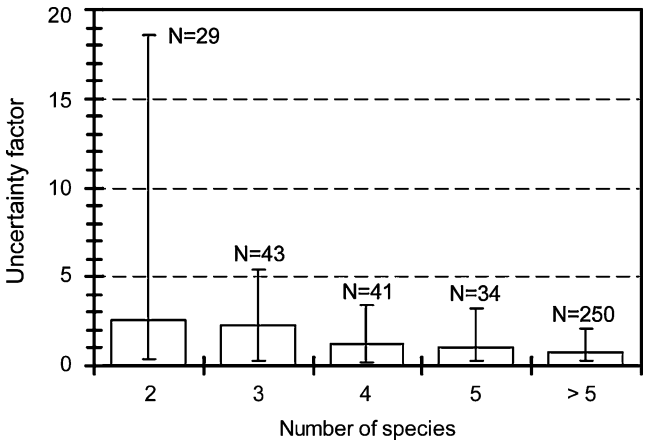

Fig. 3 Uncertainty in chemical-specific toxic potency (∂TU/∂C) for varying number of species on the basis of which ecotoxicity parameters were derived, expressed as the logarithm of the 95th percentile divided by the fifth percentile of the uncertainty distribution. The *columns* represent the median uncertainty factor of all pesticides with the same number of species, and the *whiskers* represent the fifth and 95th percentiles of all uncertainty factors calculated. *N* indicates the number of pesticides included

Uncertainty in the toxic potency (∂TU/∂C) is fully related to uncertainty in μ_x, the median sensitivity of species for pesticide x, which depends on the number of species tested (n_s) and the chemical-specific spread in species sensitivity tested for pesticide x (σ_x). For most pesticides (250), toxicity data were available for more than five species. Figure 3 shows uncertainty in toxic potency regarding to the number of species on the basis of which ecotoxicity parameters were derived. Average uncertainty in toxic potency for pesticides with n_s=2 is 2.6 orders of magnitude and uncertainty decreases with increasing n_s to around one order of magnitude for $n_s \geq 4$. Most toxicity data were available on invertebrates and ectotherm vertebrates. Of all 6,701 toxicity tests included, 44% were performed on each of these species groups. Only 2% of data were on bacteria, archaea, and protista and 10% on plants and fungi. Uncertainty distributions of all 397 chemical-specific effect factors are listed in the Electronic Supplementary Material.

Figure 4 presents the uncertainty of ecotoxicological effect factors of pesticides specified per TMoA. The columns represent median uncertainty factors of all pesticides caused by uncertainty in the TMoA-specific and chemical-specific parts of the effect factor. The whiskers show variation in uncertainty ranges of pesticides within a TMoA mainly caused by uncertainty in the chemical-specific toxic potency. Overall, the largest uncertainties were reached for inhibitors of amino acid synthesis (IAS) due to a large uncertainty in the chemical-specific toxic potency. Uncertainty distributions of all 397 ecotoxicological effect factors are listed in the Electronic Supplementary Material.

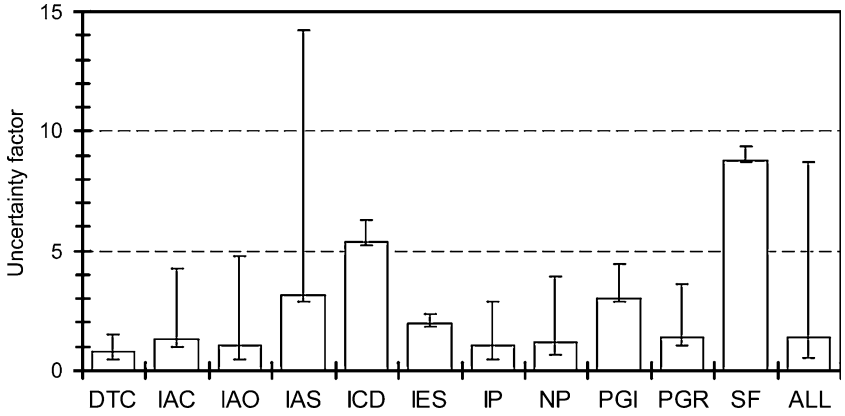

Fig. 4 Uncertainty in ecotoxicological effect factors (∂msPAF/∂C) per toxic mode of action, expressed as the logarithm of the 95th percentile divided by the fifth percentile of the uncertainty distribution. The *columns* represent the median uncertainty factor of all pesticides within one TMoA, and the *whiskers* represent the fifth and 95th percentiles of all uncertainty factors calculated

Figure 5 shows two ranges of uncertainty in ecotoxicological effect factors of pesticides within a major TMoA. Uncertainty ranges are divided in uncertainty that is attributed to the TMoA-specific part of the effect factor only (depending on TMoA-specific spread in species sensitivity (σ_j), concentration (C_x), and multisubstance potentially affected fraction (msPAF)) and uncertainty in average species sensitivity (μ_x), which is attributed to both parts of the effect factor. Uncertainty in average species sensitivity dominates for each pesticide within DTC, inhibitors of photosynthesis (IP), and plant growth regulators. The TMoA-specific part of the effect factor dominates overall uncertainty for each pesticide acting as inhibitors of cell division and as SF. For pesticides belonging to the other major TMoAs, it depends on the number of species toxicity data are based on, in combination with the chemical-specific spread in species sensitivity, whether uncertainty is dominated by the TMoA-specific part of the effect factor or by average species sensitivity.

4 Discussion and conclusions

In the previous paper on HPVCs (Van Zelm et al. 2007), several aspects in the model limitations and the results were discussed that account for pesticides as well since we applied the same method and model. Therefore, in "Section 4.1" and "Section 4.2", only the aspects that differ from HPVCs are discussed, and results for pesticides are stressed and compared to results for HPVCs. "Section 4.3" subsequently addresses the current work in an LCA context.

4.1 Model limitations

In the present study, effect factors were calculated from steady-state concentrations of average pesticide emissions, based on assumed representative emissions for 1 year (2004). As pesticide application is season dependent, emissions vary during the year and they may vary over

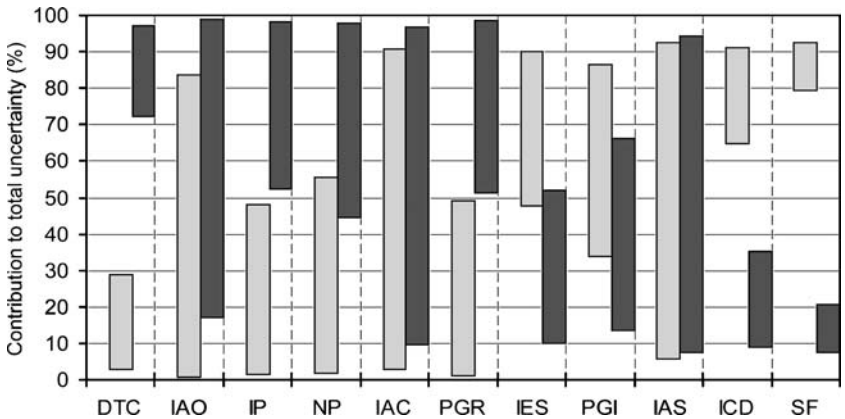

Fig. 5 Ranges of contribution to uncertainty (%) in estimated ecotoxicological effect factors for all pesticides within a toxic mode of action. The *light gray stacks* include uncertainty of TMoA-specific spread in species sensitivity (σ_j), concentration (C_x), and multisubstance potentially affected fraction of species. The *dark gray stacks* indicate uncertainty ranges of average species sensitivity (μ_x)

the years as well. A real steady-state situation is thus unlikely to occur.

Furthermore, the choice for a specific region to obtain background concentrations can be important. As a sensitivity analysis, we checked the influence of increasing and decreasing background concentrations of the pesticides included in this work on the effect factors. Median effect factors for sites with ten times higher background concentrations are up to a factor of 3 lower for DTC, inhibitors of acetylcholinesterase organophosphates (IAO), IP, and pyrethroid neurotoxicants compared to the current background situation. Median effect factors for the other TMoAs will increase up to a factor of 7, except for the SF effect factors, which increased two orders of magnitude. Effect factors for sites with a ten times lower background concentration will be up to a factor of 2 higher for DTC and IP. For all other TMoAs, median effect factors decrease for lower background concentrations, from a factor of 1.3 for IAO up to 3.5 orders of magnitude for SF.

For the variation in uncertainty in ecotoxicological effect factors for different background concentrations, two main trends can be observed: (1) uncertainty in ∂msPAF/∂C decreases with increasing pollution and, (2) for TMoAs with a large uncertainty range as calculated in this study, the decrease in uncertainty is larger than for TMoAs with a small uncertainty range. So, uncertainty in effect factors for DTC does not decrease for a tenfold increase in background concentration, while uncertainty in effect factors for SF decreases the most (see Table A2 in the supporting information for current uncertainty ranges).

To demarcate the findings, several choices were made regarding the input ecotoxicity data. First, although Larsen and Hauschild (2007b) recommended in their GM-troph method to base the ecotoxicological effect factor equally on three trophic levels represented by algae, crustaceans, and fish, we chose to derive SSDs on the basis of data for individual species. A reason for this is that data for every pesticide toxicity on each of the three trophic levels were not available. The Electronic Supplementary Material shows that toxicity data were available on different species groups, although mostly for invertebrates and ectotherm vertebrates. Second, average toxicity values were estimated with acute median-effect toxicity data (EC50). Application of chronic toxicity data may change the results (effect factor values), as chronic exposure of specific chemicals influences growth and reproduction differently (at lower concentrations) than acute exposure. There were less chronic data available, and acute-to-chronic conversion would introduce extra uncertainties. Because acute toxicity is directly proportional to chronic toxicity (De Zwart 2002), we chose to use acute toxicity data in our analysis. Moreover, using SSDs based on EC50s has a clearer intuitive ecological implication since EC50 exceedance is likely to imply visible acute effects in the field, while NOEC exceedance does not (see, e.g., Posthuma and De Zwart 2006).

4.2 Interpretation of results

We used the toxic pressure assessment method, based on msPAF quantification using SSDs, to calculate freshwater ecotoxicological effect factors and their uncertainties for 397 pesticides, which represent 11 pesticide-specific toxic modes of action. The ecotoxicological effect factor calculations consist of a TMoA-specific part and the chemical-specific toxic potency, for which an uncertainty analysis was performed. Taking into account the model limitations as described above, the meaning of obtained results is discussed in this paragraph.

Figure 2 shows that TMoAs with the largest uncertainties in the TMoA-specific part (∂msPAF/∂TU) have low median ∂msPAF/∂TU values. Van Zelm et al. (2007) showed that for low spreads in toxicity between species, especially in combination with low ambient toxic pressure, uncertainty in ∂msPAF/∂TU is relatively large. This larger uncertainty is caused by the nonlinearity of the SSD curve: at low effective toxicity, the change in toxic pressure (PAF) following a change in toxicity is much larger than following the same change in toxicity at higher effective toxicity values. This is particularly the case for systemic fungicides. To decrease uncertainty in σ_j and PAF_j, more pesticides should be included in ∂msPAF/∂TU calculations for these TMoAs. Due to the apparent greater toxicity of pesticides compared to chemicals included in the research by Van Zelm et al. (2007), smaller uncertainty ranges were obtained for the TMoA-specific parts of the effect factor for pesticide-specific TMoAs than for nonspecific TMoAs.

Contrary to what Van Zelm et al. (2007) found for HPVCs, uncertainty in predicted ambient pesticide concentrations contributes for a minor part to uncertainty in ∂msPAF/∂TU. This is due to the fact that more reliable emission data were available for pesticides than for HPVCs (Harbers et al. 2006; Henning-de Jong et al. 2008).

Uncertainty in the toxic potency, ∂TU/∂C, depends on the number of species for which toxicity data were available. Uncertainty ranges calculated for the toxic potency per number of species are in-line with previous research (Aldenberg and Jaworska 2000; Van Zelm et al. 2007). We found that the variation in uncertainty in effect factors substantially decreases for pesticides for which toxicity was tested on more than two species (see Fig. 3). The 95th percentile of the uncertainty distribution decreases from 19 orders of magnitude for $n=2$ to five orders of magnitude for $n=3$.

The variation in median ecotoxicological effect factors of all pesticides covers a range of up to nine orders of magnitude. When this range is compared to uncertainty in

ecotoxicological effect factors, it can be seen whether the applied method is useful to calculate an ecotoxicological effect factor for an individual pesticide. Figure 4 shows that only for pesticides within IAS and SF uncertainty can exceed nine orders of magnitude. As average uncertainty for all pesticides is 1.4 orders of magnitude and the 95th percentile is below nine orders of magnitude, calculation of individual effect factors for comparison between TMoAs is considered useful.

4.3 Relevancy in LCA

We provide TMoA-specific effect factors and their uncertainties for 11 TMoAs. For other pesticide-specific TMoAs, no TMoA-specific effect factor could be calculated due to lack of data. These TMoAs include cyclodiene-type neurotoxicants, such as lindane. As a first start, our calculated weighted-average TMoA-specific factor for these TMoAs, with its 90% confidence interval, can be used as a substitute.

Ecotoxicological effect factors are divided in a TMoA-specific and a chemical-specific part. This division enables practical comparison in an LCA of pesticides with the same TMoA, as solely the chemical-specific part has to be investigated. This is particularly helpful for pesticides belonging to a TMoA with a low spread in toxicity between species and/or low effective toxicity, as our study shows that this has a large influence on uncertainty in the TMoA-specific part of the effect factor.

The effect factor is one part of ecotoxicological characterization factors, and so is uncertainty in it. Huijbregts et al. (2003) applied an uncertainty range (90% CI) of a factor of 85 for the fate factor, as derived from Huijbregts et al. (2000). This uncertainty range was based on three chemicals only. To our knowledge, no studies are available that quantify parameter uncertainty in the fate factor for a large set of chemicals. We calculated a median 90% CI for the effect factor of 26, which can be up to an uncertainty factor of eight orders of magnitude. To put this uncertainty in effect factors into perspective within LCIA, more information on the uncertainty in fate factors needs to be derived.

The linear dose–response method to derive ecotoxicological effect factors, as outlined by Payet (2004) and Pennington et al. (2004), assumes a value of 0.5 where we calculate a TMoA-specific effect factor, ∂msPAF/∂TU. The four TMoAs with the lowest uncertainty range for ∂msPAF/∂TU (see Fig. 2) have ∂msPAF/∂TU values above 0.5. This shows that the use of the linear dose–response method to derive ecotoxicological effect factors for pesticides may result in underestimation of ecotoxic damage for these groups of pesticides up to a factor of 3 for pyrethroid neurotoxicants and inhibitors of acetylcholinesterase (organophosphates). Moreover, ∂msPAF/∂TU for five TMoAs is lower in our research compared to the linear dose–response method and up to nine orders of magnitude for systemic fungicides. However, uncertainty in ∂msPAF/∂TU is relatively small compared to uncertainty in ∂TU/∂C (see Fig. 4).

From a conceptual point of view, the nonlinear method can be preferred as it describes reality better. The applied msPAF method allows for addressing nonlinear concentration–response relationships. However, the applied nonlinear method is clearly more complex than the linear method. For additional complexity to be justified, characterization factors from the complex method should be more accurate than those from the simplistic method. Model uncertainty is larger in the linear method (Pennington et al. 2004) but is difficult to quantify, whereas parameter uncertainty will be larger in the nonlinear method. It is important to give LCA practitioners a good insight in uncertainties to help them make carefully thought-out decisions. The applied nonlinear method provides the possibility to quantify parameter uncertainty in the TMoA-specific part of the ecotoxicological effect factor.

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